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METHOD FOR THE MANUFACTURE OF A RAW MATERIAL POWDER FOR A  
CAPACITOR MATERIAL

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### Claim

A method for the manufacture of a raw material powder for a capacitor material characterized by the fact that, during the manufacture of the raw material powder of a solid solution of a composite oxide with a perovskite structure (to be called perovskite hereafter) represented by the general formula  $(\text{Ba}_{1-x}\text{A}_x)\text{Ti}_{1-y}\text{B}_y\text{O}_3\text{-aMO}$  (where A represents one or more metals selected from Pb, Ca, Sr, Ce and La, B represents one or more metals selected from Zr, Sn, Zn, Nb, Mg, Ni and Co, MO represents one or more metal oxides selected from oxides of Mn, Nb, Ta, Co and Al,  $0 \leq x < 1$ ,  $0 \leq y < 0.5$ , and  $0 < a < 0.2$ ) and a metal oxide, a  $\text{BaTiO}_3$  powder with a particle diameter of 0.1-1  $\mu\text{m}$  is suspended in a liquid phase, then a solution and/or a suspension of the remaining various components is contacted with a precipitate-forming liquid, and after the sequential formation of the precipitate, the precipitate obtained is calcined.

### Detailed explanation of the invention

#### Industrial application field

The present invention relates to a method for the manufacture of a raw material powder of a solid solution of a perovskite and a metal oxide for use in a capacitor material. Conventionally, solid solutions of perovskite and metal oxide have been utilized as capacitor materials in a wide range [of applications]. Recently, it has been desirable to raise this function to a high level. A raw material powder of a solid solution of a perovskite and a metal oxide with good sintering characteristics, uniformity, and a high bulk density at a low cost in response to this demand has been highly desirable.

#### Prior art and its problems

Conventionally, the dry method of manufacturing solid solutions of perovskite and metal oxide has been used. The following two procedures are available.

(1) A perovskite powder is synthesized by the dry type method, the coprecipitation method or the like, then the perovskite powder and a metal oxide powder are mixed in a dry method, and the mixture is calcined.

(2) Compounds of constituent raw material components of perovskite and a metal oxide powder are mixed in a dry method, and the mixture is calcined.

However, in any of the methods, it is difficult for the powder obtained to be uniform in composition and an excellent performance is difficult to obtain. Furthermore, the particle diameters of the powder are large, and sintering characteristics are also insufficient.

#### Objective of the invention

The objective of the present invention is to provide a method capable of eliminating the disadvantages of the conventional dry type method and, furthermore, a wet method capable of manufacturing, at a high efficiency, a raw material powder of a solid solution of perovskite and a metal oxide having good sintering characteristics, uniformity, a low cost, a high bulk density, and providing high performance.

#### Technical means to solve the problems

As a result of zealous investigations in order to achieve the objective described previously, the present inventors accomplished the present invention.

The present invention relates to a method for the manufacture of a raw material powder for a capacitor material characterized by the fact that, during the manufacture of the raw material powder of a solid solution of a composite oxide with a perovskite structure (to be called perovskite hereafter) represented by the general formula  $(\text{Ba}_{1-x}\text{A}_x)\text{Ti}_{1-y}\text{B}_y\text{O}_3\text{-aMO}$  (where A represents one or more metals selected from Pb, Ca, Sr, Ce and La, B represents one or more metals selected from Zr, Sn, Zn, Nb, Mg, Ni and Co, MO represents one or more metal oxides selected from oxides of Mn, Nb, Ta, Co and Al,  $0 \leq x < 1$ ,  $0 \leq y < 0.5$ , and  $0 < a < 0.2$ ) and a metal oxide, a  $\text{BaTiO}_3$  powder with a particle diameter of  $0.1\text{-}1\ \mu\text{m}$  is suspended in a liquid phase, then a solution and/or a suspension of the remaining various components is contacted with a precipitate-forming liquid, and after the sequential formation of the precipitate, the precipitate obtained is calcined.

In the solid solution of a composite oxide with a perovskite structure (to be called perovskite hereafter) represented by the general formula  $(\text{Ba}_{1-x}\text{A}_x)\text{Ti}_{1-y}\text{B}_y\text{O}_3\text{-aMO}$ , Component A is one or more metals selected from Pb, Ca, Sr, Ce and La, B is one or more metals selected from Zr, Sn, Zn, Nb, Mg, Ni and Co, MO is one or more metal oxides selected from oxides of Mn, Nb, Ta, Co and Al,  $0 \leq x < 1$ ,  $0 \leq y < 0.5$ , and  $0 < a < 0.2$ . Preferably, y is not greater than 0.5 nor is a greater than 0.2, since this results in problems with the characteristics.

In the capacitor material with  $\text{BaTiO}_3$  shown in the previously given general formula as the major component, the solid solution state of Component A in Ba, the solid solution state of Component B in Ti, and the solid solution state of MO in  $\text{BaTiO}_3$  render major effects on the dielectric constant of the capacitor and the temperature dependence of the dielectric constant. Furthermore, it has been known that the particle shape and the crystal state of  $\text{BaTiO}_3$  affect the solid solution states of these components.

In the present invention, electrical characteristics can be improved by using a  $\text{BaTiO}_3$  powder having a perovskite structure with a particle diameter of 0.1-1  $\mu\text{m}$ .

The  $\text{BaTiO}_3$  powder of the present invention is obtained by contacting a solution of the component Ba and the component Ti with a precipitate-forming liquid by a wet type method to form a precipitate, and subjecting this to a heat treatment greater than 1000°C; or by mixing oxides of Ba and Ti in a dry type method, and subjecting this to a heat treatment greater than 1000°C, and then pulverizing it to a size less than 1  $\mu\text{m}$ .

In the present invention, the  $\text{BaTiO}_3$  powder mentioned previously is dispersed sufficiently in the liquid phase. The solution and/or the suspension of the remaining various components are contacted with a precipitate-forming liquid, to form a precipitate sequentially. In this case, excess Ba or Ti component is also precipitated. There are no special restrictions on the compounds of the various components for the preparation of the solution and/or the suspension of the various components. They can be selected appropriately from their hydroxides, carbonates, oxy salts, sulfates, nitrates, chlorides or other inorganic salts, acetates, oxalates or other organic salts, oxides, etc. These are generally used as aqueous solutions. In the case in which they are not soluble in water, they can be made soluble by the addition of an acid. For insoluble raw materials, they can also be used as suspension solutions. Furthermore, instead of an aqueous solution, an alcohol solution can also be used.

As the precipitate-forming liquids, solutions of ammonia, ammonium carbonate, ammonium bicarbonate, oxalic acid, ammonium oxalate, caustic alkali, alkylamine, and so on can be mentioned. As the alkylamines, methylamine, ethylamine, propylamine, butylamine, or other primary amines having lower alkyl groups, cyclohexylamine or other primary amines, dimethylamine, diethylamine or other secondary amines having lower alkyl groups, and triethylamine or other tertiary amines having lower alkyl groups can be mentioned.

In the present invention, in the  $\text{BaTiO}_3$  powder with a particle diameter of 0.1-1  $\mu\text{m}$ , a solution and/or a suspension of the remaining various components is contacted with a precipitate-forming liquid to cause the sequential formation of the precipitate. By the precipitation of the remaining various components in the  $\text{BaTiO}_3$  powder in this manner, the shapes of the primary particles of the various precipitates are not uniform. However, the shapes of secondary particles in agglomerate form are uniform. Furthermore, the sizes of the secondary

particles are appropriate particle diameters of the submicron order or so, and these are materials with good dispersibility.

In the formation of the precipitate of the remaining various components, while the precipitate-forming liquid is being stirred, the solution and/or the suspension of the remaining components may be added to the precipitate-forming liquid or the addition may be conducted in the opposite way. The addition is preferably carried out while the liquid is being stirred sufficiently.

Furthermore, during the formation of the precipitate, it is also acceptable that, for example, water washing is carried out in order to remove anions after the formation of the precipitate of one of the components. The precipitate is then dispersed in fresh water or alcohol. The solution of other components and the precipitate-forming liquid are further added to form the precipitate.

After the precipitate obtained by the method described above has been washed with water or the like according to a conventional washing method, filtered and dried, it is then calcined. The drying can be conducted under atmospheric pressure or under a reduced pressure.

If the calcination temperature is too low, the dewatering and the pyrolysis of the precipitate will be insufficient. Furthermore, if it is too high, the powder will become coarse. In general, the calcination temperature is appropriately in the range of 500-1200°C.

#### Application examples

The present invention will be explained in further detail with the following application examples and comparative examples.

##### Application Example 1

$\text{BaTiO}_3\text{-}0.03\text{Nb}_2\text{O}_5\text{-}0.02\text{Co}_2\text{O}_3$

37.8 g of oxalic acid were dissolved in 1000 mL of water, and 100 mL of a 28% ammonia aqueous solution were further added. To this, a solution obtained by the dissolution of 49.66 g of barium nitrate  $[\text{Ba}(\text{NO}_3)_2]$  in 1000 mL of water and a solution obtained by the dissolution of 54.00 g of titanium tetraisopropoxide  $[\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4]$  in 500 mL of ethanol were added with stirring. The precipitate obtained was filtered and washed. After drying, it was subjected to a heat treatment at 1000°C. The powder obtained exhibited a perovskite structure. The particle diameter was 0.3  $\mu\text{m}$ .

This powder was suspended in water. Furthermore, a solution obtained by the dissolution of 3.2419 g of niobium pentachloride ( $\text{NbCl}_5$ ) in 100 mL of ethanol was added with stirring.

The precipitate obtained was washed by repeated decanting with 3 L of ion-exchanged water five times. Next, a solution obtained by the addition of 7.5 g of diethylamine in 100 mL of

water was added to the solution containing the precipitate. Furthermore, water was added to 1.5 L. Moreover, a solution obtained by the dissolution of 2.3280 g of cobalt nitrate  $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$  in 100 mL of water was added dropwise with stirring. This precipitate was washed with ion-exchanged water. After filtration and drying, it was calcined at  $900^\circ\text{C}$  for 2 h. The powder obtained was observed under a transmission electron microscope. It was a uniform material with a particle diameter of approximately  $0.5\ \mu\text{m}$  and the particle size distribution was narrow.

Polyvinyl alcohol was added to this powder at 0.8 wt % and molding was carried out at  $1\ \text{t}/\text{cm}^2$ . It was then fired at  $1300^\circ\text{C}$  for 2 h. The density of the sintered body obtained was  $5.9\ \text{g}/\text{cm}^3$ . Moreover, this sintered body was coated with a silver paste and then baked at  $600^\circ\text{C}$ . The electrical characteristics were measured at room temperature. The specific dielectric constant was 3350,  $\tan \delta$  0.52%, and the temperature characteristic of the specific dielectric constant in the range of  $-25^\circ\text{C}$  to  $+125^\circ\text{C}$  was +10 to -12% with the value at  $25^\circ\text{C}$  as the reference. Furthermore, the transverse rupture strength of the sintered body was measured to be  $1200\ \text{kg}/\text{cm}^2$ . The size of the granular boundary of the sintered body was  $5\ \mu\text{m}$ .

#### Comparative Example 1

37.95 g of titanium oxide ( $\text{TiO}_2$ ), 93.74 g of barium carbonate ( $\text{BaCO}_3$ ), 3.9872 g of niobium oxide ( $\text{Nb}_2\text{O}_5$ ) and 1.6586 g of cobalt oxide ( $\text{Co}_2\text{O}_3$ ) were weighed so that the composition was the same as that in Application Example 1. Water was added. After sufficient mixing with a ball mill, filtration and drying were carried out. The composition was calcined at  $1150^\circ\text{C}$  for 2 h. The particle diameter of the powder obtained was about  $3\ \mu\text{m}$ , and with a particle size distribution of  $0.5\text{--}5\ \mu\text{m}$ . Next, this powder was molded and fired in the same manner as in Application Example 1. The electrical characteristics of the sintered body obtained were measured. The specific dielectric constant was 2150,  $\tan \delta$  1.3%, and the temperature characteristic of the specific dielectric constant was +24 to -13%. The density of the sintered body obtained was  $5.65\ \text{g}/\text{cm}^3$ . The transverse rupture strength was  $780\ \text{kg}/\text{cm}^2$ . The size of the granular boundary of the sintered body was  $15\ \mu\text{m}$ .

#### Comparative Example 2

110.79 g of commercial barium titanate ( $\text{BaTiO}_3$ ) (particle diameter  $2\ \mu\text{m}$ ), 3.9872 g of niobium oxide ( $\text{Nb}_2\text{O}_5$ ) and 1.6586 g of cobalt oxide ( $\text{Co}_2\text{O}_3$ ) were weighed so that the composition was the same as that in Application Example 1. These were mixed, calcined, molded and fired in the same manner as in Comparative Example 1. The electrical characteristics of the sintered body obtained were measured. The specific dielectric constant was 1870,  $\tan \delta$  1.2%, and the temperature characteristic of the specific dielectric constant was +20 to -17%. The

density of the sintered body obtained was 5.60 g/cm<sup>3</sup>. The transverse rupture strength was 750 kg/cm<sup>2</sup>. The size of the granular boundary of the sintered body was 11 μm.

Table 1

①	例	② 組成
③	実施例 2	Ba 0.93Sr 0.07Ti O <sub>3</sub> -0.03Ta <sub>2</sub> O <sub>5</sub> -0.02Mn O <sub>2</sub>
④	比較例 3	
③	実施例 3	Ba 0.90Ce 0.10Ti O <sub>3</sub> -0.03Mn O <sub>2</sub>
④	比較例 4	
③	実施例 4	Ba 0.92Pb 0.08Ti 0.0Zr 0.1O <sub>3</sub> --0.03Al <sub>2</sub> O <sub>3</sub>
④	比較例 5	
③	実施例 5	Ba 0.93Ca 0.07Ti 0.93Sn 0.07O <sub>3</sub> -0.03Nb <sub>2</sub> O <sub>5</sub> -0.02Co <sub>2</sub> O <sub>3</sub>
④	比較例 6	
③	実施例 6	Ba 0.90Ca 0.10Ti 0.9Co 0.03Nb 0.07O <sub>3</sub> --0.03Mn O <sub>2</sub>
④	比較例 7	
③	実施例 7	Ba 0.85Sr 0.15Ti 0.8Zn 0.07Nb 0.13O <sub>3</sub> --0.03Mn O <sub>2</sub>
④	比較例 8	
③	実施例 8	Ba 0.85Ca 0.15Ti 0.9Ni 0.015Co 0.015Nb 0.07O <sub>3</sub> --0.03Al <sub>2</sub> O <sub>3</sub>
④	比較例 9	
③	実施例 9	Ba 0.96La 0.04Ti 0.9Co 0.03Nb 0.07O <sub>3</sub> -0.03Mn O <sub>2</sub>
④	比較例 10	
③	実施例 10	Ba 0.94Ce 0.06Ti 0.9Mn 0.04Nb 0.06O <sub>3</sub> --0.03Co <sub>2</sub> O <sub>3</sub>
④	比較例 11	

Key: 1 Example  
 2 Composition  
 3 Application Example  
 4 Comparative Application Example

#### Application Examples 2 through 10

The materials with the compositions shown in Table 1 were prepared in the same manner as in Application Example 1. The results of evaluating the characteristics of the powders and the sintered bodies obtained are shown in Table 2.

#### Comparative Examples 3 through 11

The compositions corresponding to those in Application Examples 2 through 10 were prepared in the same manner as in Comparative Example 1 by the dry type method. The results of evaluating the characteristics of the powders and the sintered bodies obtained are shown in Table 2.



Table 2

① 例	② 平均 粒径 μm	③ 烧结 温度 ℃	④ 密度 g/cm <sup>3</sup>	⑤ 比誘 電率	tan δ (%)	⑥ 抗折力 強度 kg/cm <sup>2</sup>	⑦ 温度特性 -25~125℃	⑧ 烧结体 粒界寸法 μm
⑨ 実施例 2	0.2	1300	5.8	3400	0.7	1220	+7~-11	5
比較例 3	3.5	"	5.5	3240	3.8	690	+25~-15	13
⑨ 実施例 3	0.4	"	5.9	5600	0.8	1150	+10~-14	4
比較例 4	3.0	"	5.6	4230	3.7	650	+30~-18	20
⑨ 実施例 4	0.4	1250	6.1	3450	0.4	1290	+6~-10	3
比較例 5	2.5	"	5.8	3060	4.5	720	+22~-16	10
⑨ 実施例 5	0.5	1300	5.8	3750	0.5	1300	+8~-9	6
比較例 6	3.5	"	5.4	3250	2.3	700	+33~-20	18
⑨ 実施例 6	0.6	1250	6.0	4500	0.9	1250	+11~-10	5
比較例 7	2.0	"	5.7	4280	5.1	620	+28~-20	15
⑨ 実施例 7	0.4	"	6.1	4350	1.0	1180	+10~-8	3
比較例 8	2.5	"	5.6	4050	4.4	550	+22~-25	21
⑨ 実施例 8	0.5	"	6.0	4450	1.1	1170	+12~-9	4
比較例 9	3.0	"	5.6	4120	2.8	650	+26~-17	10
⑨ 実施例 9	0.5	1300	5.9	3620	0.8	1150	+10~-11	5
比較例 10	2.0	"	5.5	3150	2.6	810	+25~-18	15
⑨ 実施例 10	0.6	"	5.9	4250	0.7	1210	+12~-10	4
比較例 11	3.5	"	5.4	3760	1.9	750	+20~-17	18

- Key:
- 1 Example
  - 2 Average particle diameter
  - 3 Firing temperature
  - 4 Density
  - 5 Dielectric constant
  - 6 Transverse rupture strength
  - 7 Temperature characteristic
  - 8 Sintered body granular boundary dimensions
  - 9 Application Example
  - 10 Comparative Example

#### Effect of the invention

During the manufacture of the raw material powder of a solid solution of perovskite represented by the general formula  $(Ba_{1-x}A_x)Ti_{1-y}B_yO_{3-a}MO$  (where A represents one or more metals selected from Pb, Ca, Sr, Ce and La, B represents one or more metals selected from Zr, Sn, Zn, Nb, Mg, Ni and Co, MO represents one or more metal oxides selected from oxides of Mn, Nb, Ta, Co and Al,  $0 \leq x < 1$ ,  $0 \leq y < 0.5$ , and  $0 < a < 0.2$ ) and a metal oxide, a  $BaTiO_3$  powder with a particle diameter of 0.1-1  $\mu m$  is suspended in a liquid phase, then a solution and/or a suspension of the remaining various components is contacted with a precipitate-forming liquid to cause the sequential formation of the precipitate. In doing this, agglomeration during precipitate formation or coagulation during drying or calcination does not occur. A powder

having a high bulk density and good sintering characteristics, and providing a high performance can be manufactured with good reproducibility.

Furthermore, in the present process, the various phases are mutually dispersed to a large extent. Therefore, the material obtained by the calcination of this substance has a narrow particle size distribution. The particles are also uniform. Therefore, a sufficient uniformity in composition is achieved. Due to the fact that the process is simple, a powder having a good reproducibility, a low cost and good sintering characteristics, and providing a high performance can be obtained, and other excellent effects are available.